Trace elements enrichment of coastal sediments near geological complexes: the relevance of defining proxies to element normalization

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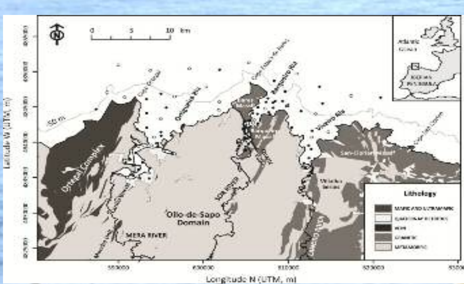
Sediment contamination by trace elements (TEs) is usually estimated by comparison to natural levels at uncontaminated reference sites or to Earth' Crust composition [1]. Enrichment factors are calculated by dividing concentrations normalized to Al, Fe, Li or Sc to preindustrial values [2, 3, 4]. However, coastal sediments could be naturally enriched by TEs from nearby geochemical domains inshore [5]. Identification of proxies to select the best normalization element is crucial to distinguish between natural enrichment from anthropogenic derived contamination. We examine this problematic from the coastal sediments nearby the geological complex of Cape Ortegal at NW of the Iberian Peninsula (SW Europe).

Ortegal Chromites

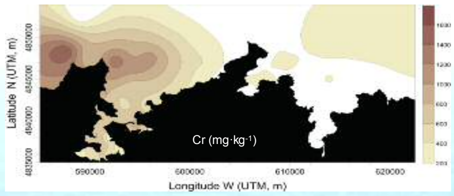
The northern coast of Galicia includes the Ortigueira, Barqueiro and Viveiro Rias and the Capes Ortegal and Estaca-de-Bares, the northernmost point of the Iberian Peninsula, surrounded by different geological domains (Fig.1). The Cape Ortegal includes the Ortegal allochthonous complex with abundant ultramafic rocks and metaigneous granulites, lower metamorphic facies with pyroxenes, eclogites, amphibolite and serpentinites [6]. Minerals incorporated in these rocks with high content of Cr and Ni are chromite and chromospinel (Cr), gersdorfite and pentlandite (Ni) [7]. Eastward, lithology is dominated by a relative autochthon rocks composing the series occupying the Ollo de Sapo Domain, which is characterized by metamorphic (mainly gneisses) and granite-type rocks [8].

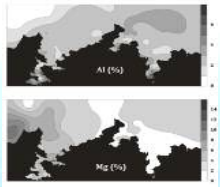


One hundread and three sediments were sampled in July 2007 using Van Veen grabs. The topmost layer (0–1 cm) was taken with a plastic spatula, stored in pre-cleaned LDPE vials and kept at 4°C; later oven dried at 45±5°C; sandy and muddy fraction was separated with a 2 mm sieve (Retsch AS200), homogenized and ground with an agate mortar for analysis.

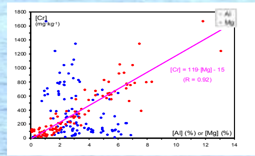
Around 100 mg of each sample were completely digested with HF and Aqua Regia in closed Teflon bombs at 100°C for 1 h. Major and minor elements were analyzed by FAAS on a Perkin Elmer AA100 with a nitrous oxide-acetylene flame (Al, Si Ca and Mg) and air-acetylene flame (Fe and Mn). Trace elements (V, Cr, Co, Ni, Cu, Zn, As, Mo, Cd, Pb and U) were determined using a quadrupole ICP-MS (Thermo Elemental, X-Series). The precision and accuracy of the analytical procedures was controlled through CRM analysis (MAG-1 and PACS-2; NRCC). The obtained concentrations were not different from certified values (t-student; α=0.05).

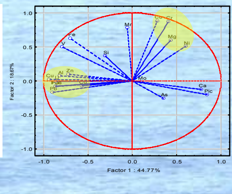
The grain size distribution in sediment samples pointed to the predominance of sand in the shelf (94±6%) while fine-grained material was only present in samples from the innermost part of Rias. Aluminium ranged from 1-5% (sandy shelf) to 7% (muddy inner ria). No significant relationships (p>0.05) were found between Al content and the grain size indicating that sediment nature is not fully explained by the variation of aluminosilicates minerals. Elevated Mg contents were found in the shelf sediments around Cape Ortegal (max. 13%); Mg decreased towards the inner rias: 2-8% (Ortigueira), 0.6-2.1% (Barqueiro) and 0.1-1.8 % (Viveiro).

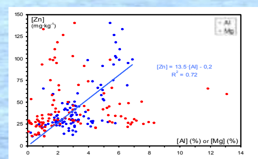




Spatial distribution patterns of Cr, Ni and Co were similar to Mg, showing elevated values in sediments surrounding the Cape Ortegal, where Cr (760-1670 mg·kg⁻¹) decreased gradually eastward shelf and landward rias. Similarly pattern was observed to Ni that varied within two orders of magnitude, from 75 to 1360 mg·kg⁻¹. Cobalt content in shelf sediments also mimics the Mg with a gradual decrease from Cape Ortegal to east (70-4.7 mg·kg⁻¹ in the shelf) and to the ria heads, down to 1.1 mg·kg⁻¹ at Barqueiro.







PCA analysis grouped Mg, Cr, Ni and Co together. This association points to Mg as a proxy of the geological complex in coastal sediments [5]. Contents of Cr, Ni and Co in the sediments of surveyed area showed no significant correlations (p>0.05) with Al and they are not associated with aluminosilicates. Conversely, significant correlations (p<0.05) were found with Mg vs. Cr, Ni and Co pointing to the similar origin of the four aforementioned elements [9].

Normalization to Mg is proposed to interpret the natural enrichment of these elements while the remaining metals and As were mainly associated to Al. Element-Al relationships indicate a moderate contamination of Cu, Pb and Zn in the fishing harbor of Viveiro Ria mainly.

The results point out the influence of the Ortegal Complex on the distribution of Cr, Ni and Co in surface sediments of that coastal region. In the boundary environments where lithogenic and anthropogenic contributions joined, geological complexes, such as the Cape Ortegal, increases the land-sea exchange of trace metals. Therefore, metal enrichment in sediments due to natural features should be carefully considered in the application of contamination status definition and UE Marine Strategy Framework Directives.

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We thank the crew and staff of INTERESANTE project cruises on board the IEO R/V Lura and CSIC R/V Mytilus for their kind assistance during the field sampling and laboratory analysis. This study was supported by the research projects INTERESANTE (ref. CTM2007-62546-C03/MAR) and MITOFE (ref. CTM2011-28792-C02) financed by CICYT and MINECO, respectively.